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AMMONIUM PHOSPHATE, MONOBASIC

[7722-76-1]

Formula: $(\text{NH}_4)\text{H}_2\text{PO}_4$; MW 115.03;

Synonyms: ammonium dihydrogen phosphate; ammonium biphosphate; primary ammonium phosphate

Uses

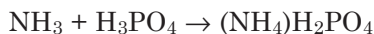
Monobasic ammonium phosphate is used in fire extinguishers; as a flame retardant for papers, plywoods, and fabrics; in baking mixtures; and in fermentation process.

Physical Properties

White crystalline powder; odorless; density 1.80 g/cm³; readily dissolves in water (40 g/ 100 g); pH of 0.2 molar solution 4.2; slightly soluble in alcohol; insoluble in acetone.

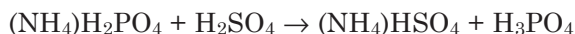
Preparation

Preparative method similar to its dibasic salt; obtained by reaction of equimolar amounts of ammonia and phosphoric acid:



Reactions

Thermal decomposition produces ammonia and phosphoric acid; reaction with sulfuric acid produces ammonium hydrogen sulfate:



$(\text{NH}_4)\text{H}_2\text{PO}_4$ decomposes under strong oxidizing conditions producing nitrogen, water, and phosphorus pentaoxide.

AMMONIUM SULFATE

[7783-20-2]

Formula: $(\text{NH}_4)_2\text{SO}_4$; MW 132.14;

Occurrence and Uses

Ammonium sulfate occurs in trace concentrations in the upper atmosphere. It is widely used as a fertilizer for rice and other crops. It is a source of sulfur for the soil. It is also used as an additive to supply nutrient nitrogen in fermentation processes (e.g., yeast production from molasses). It also is used for fireproofing timber and plastics, and in treatment of hides, and leather production.

Physical Properties

White crystalline solid; orthorhombic crystal; density 1.769 g/cm³ at 20°C; melts between 511 to 515°C (in a closed system): however, in an open system, it melts with decomposition at 280°C; readily dissolves in water (solubility, 70.6 g and 104 g per 100 g water at 0°C and 100°C, respectively); insoluble in acetone, alcohol and ether.

Thermochemical Properties

ΔH°_f	-282.5 kcal/mol
ΔG°_f	-215.6 kcal/mol
S°	52.6 cal/degree mol
C_p	44.8 cal/degree mol

Manufacture

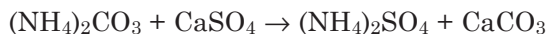
Ammonium sulfate is made by reacting synthetic ammonia (or by-product ammonia from coke-ovens) with sulfuric acid:



A mixture of ammonia gas and water vapor is introduced into a reactor ("saturator") that contains a saturated solution of ammonium sulfate and about 2 to 4% free sulfuric acid at 60°C. Concentrated sulfuric acid is added continuously to keep the solution acidic, and to retain its level at 2 to 4% free acid. The heat of reaction keeps reactor temperature at 60°C. Ammonium sulfate formed crystallizes out of its saturated solution in the reactor.

Dry, powdered ammonium sulfate may be formed by spraying sulfuric acid into a reaction chamber filled with ammonia gas. The heat of reaction evaporates all water present in the system, forming a powdery salt.

Ammonium sulfate also is manufactured from gypsum salt, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Finely divided gypsum is added to ammonium carbonate solution. Calcium carbonate precipitates out, leaving ammonium sulfate in solution.

**Reactions**

Ammonium sulfate decomposes upon heating at 100°C in an open system, forming ammonium bisulfate, NH_4HSO_4 . As a salt of a strong acid and weak base, its solution is acidic; pH of 0.1M solution is 5.5.

In aqueous solution the reactions are those of NH_4^+ and SO_4^{2-} ions. For example, addition of barium chloride, BaCl_2 precipitates out barium sulfate, BaSO_4 . The filtrate on evaporation yields ammonium chloride, NH_4Cl .

$(\text{NH}_4)_2\text{SO}_4$ forms many double salts (ammonium metal sulfates) when its solution is mixed with equimolar solutions of metal sulfates and the solution is slowly evaporated. Such double metal sulfates include ammonium cobaltous sulfate, $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2$; ferric ammonium sulfate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, ammonium nickel sulfate, $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$; and ammonium cerous sulfate, NH_4CeSO_4 .

Chemical Analysis

Elemental composition: H 6.10%, N 21.20%, O 48.43%, S 24.27%.

A small amount of solid may be dissolved in water and ammonium ion determined by the ion-selective electrode method, or miscellaneous colorimetric or titrimetric procedures (see Ammonia). Sulfate ion may be determined by ion chromatography.

AMMONIUM SULFIDE

[12135-76-1]

Formula: $(\text{NH}_4)_2\text{S}$; MW 68.143

Synonym: ammonium monosulfide

Uses

Ammonium monosulfide is used in photographic developer; to apply patina to bronze; and in textile manufacture.

Physical Properties

Unstable, decomposes at ambient temperature; forms yellow crystals below -18°C ; hygroscopic; soluble in water and alcohol, very soluble in liquid ammonia.

Thermochemical Properties

$\Delta H^\circ f$ (aq)	-55.4 kcal/mol
$\Delta G^\circ f$	-17.4 kcal/mol
S°	50.7 cal/degree mol

Preparation

$(\text{NH}_4)_2\text{S}$ is obtained from reacting hydrogen sulfide with excess of ammonia:

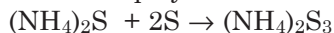


Reactions

Ammonium sulfide decomposes to ammonia and ammonium hydrosulfide:



At elevated temperatures it forms polysulfides; also, it combines with sulfur, forming ammonium polysulfide:



Ammonium sulfide forms ammonium chloride with HCl and ammonium nitrate with nitric acid, respectively.

Chemical Analysis

Elemental composition: H 11.83%, N 41.11%, S 47.05%. It may be analyzed by measuring its decomposition gaseous products, ammonia and hydrogen sulfide, either by gas chromatography using an FID or a TCD; or by selective ion electrode or colorimetric techniques.

AMMONIUM THIOCYANATE

[1762-95-4]

Formula: NH_4SCN ; MW 76.122

Uses

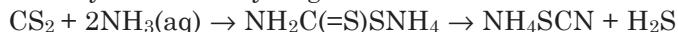
Ammonium thiocyanate is used in the manufacture of herbicides, thiourea, and transparent artificial resins; in matches; as a stabilizing agent in photography; in various rustproofing compositions; as an adjuvant in textile dyeing and printing; as a tracer in oil fields; in the separation of hafnium from zirconium, and in titrimetric analyses.

Physical Properties

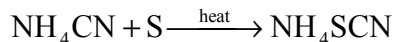
Crystalline solid forming monoclinic crystal; hygroscopic; melts at 149.6°C; decomposes at 170°C; density 1.305 g/cm³; highly soluble in water (128 g/100 mL at 0°C); soluble in liquid ammonia, alcohol, and acetone.

Manufacture

Ammonium thiocyanate is made in the United States by the reaction of carbon disulfide with aqueous ammonia. Ammonium dithiocarbamate is formed as an intermediate in this reaction, which upon heating, decomposes to ammonium thiocyanate and hydrogen sulfide.

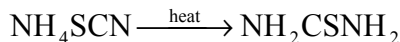


Ammonium cyanate also may be prepared by direct sulfurization of ammonium cyanide.



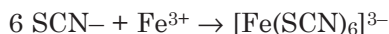
Chemical Reactions

Ammonium thiocyanate is stable in air; however, upon heating it isomerizes to thiourea:



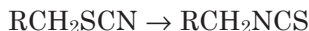
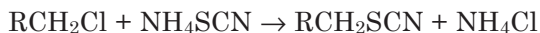
The equilibrium mixtures at 150°C and 180°C contain 30.3% and 25.3% (by weight) thiourea, respectively. When heated at 200°C, the dry powder decomposes to ammonia, hydrogen sulfide, and carbon disulfide, leaving a residue of guanidine thiocyanate [56960–89–5].

NH_4SCN is weakly acidic; reacts with caustic soda or caustic potash to form sodium thiocyanate (NaSCN) or potassium thiocyanate (KSCN). It reacts with ferric salts to form a deep-red ferric thiocyanate complex:

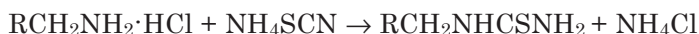


Ammonium thiocyanate reacts with several metal ions including copper, silver, zinc, lead, and mercury, forming their thiocyanate precipitates, which may be extracted into organic solvents.

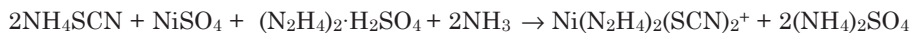
Ammonium thiocyanate reacts with alkyl halides forming alkyl thiocyanates, RSCN , which may also rearrange to alkyl isothiocyanates, RNCS :



Forms thioureas with aliphatic or aromatic amine hydrochlorides:



Ammonium thiocyanate reacts with nickel sulfate and ammoniacal solution of hydrazine sulfate forming a violet-blue crystalline precipitate:



AMMONIUM THIOSULFATE

[7783–18–8]

Formula: $(\text{NH}_4)_2\text{S}_2\text{O}_3$; MW 148.21

Uses

Two principal applications of ammonium thiosulfate are: (i) as a fertilizer blend, and (ii) in photography. It is blended with other nitrogenous fertilizers to provide sulfur to the soil. Also, the compound itself is a fertilizer; however, such applications are limited. In photography it dissolves undeveloped silver halides from negatives and prints. It is also used as a desiccant and defoliant in cotton, rice, soybean and other plants; in flue-gas desulfurization; and in

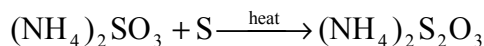
metal cleaning. It is sold as an aqueous solution, a crystal slurry, or anhydrous crystal.

Physical Properties

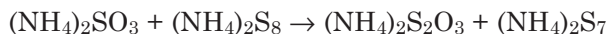
Colorless, monoclinic crystal; hygroscopic; decomposes on heating above 100°C; density 1.679 g/cm³; very soluble in water (64 g/100 g at 20°C), insoluble in alcohol, and slightly soluble in acetone.

Manufacture

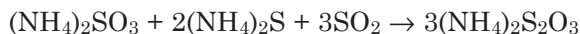
Ammonium thiosulfate is made by the reaction of ammonium sulfite with sulfur at 85 to 110°C:



or, by reacting ammonium sulfite with ammonium polysulfide:

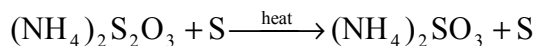


or, using sulfur dioxide and ammonium sulfide instead of ammonium polysulfide:



Reactions

When heated over 100°C, it decomposes to ammonium sulfite and sulfur:



Also, its aqueous solution decomposes slowly below 50°C.

Chemical Analysis

Elemental composition: H 5.44%, N 18.90%, O 32.39%, S 43.27%. It is dissolved in water and the aqueous solution may be analyzed for thiosulfate by titrating against a standard solution of an oxidizing agent, such as potassium dichromate or potassium permanganate. Ammonium ion in the aqueous solution may be determined by colorimetry, titrimetry, or ion-specific electrode method (see Ammonia).

ANTIMONY

[7440-36-0]

Symbol Sb; atomic number 51; atomic weight 121.75; Group VA (group 15) element; atomic radius 1.41Å; ionic radius Sb³⁺ 0.76Å; covalent radius Sb³⁺ 1.21Å; electronic configuration [Kr] 4d¹⁰5s²5p³; a metalloid element; electronegativity 1.82 (Allred-Rochow type); valence states +5, +3, 0 and -3; isotopes and natural abundance: Sb-121 (57.3%), Sb-123 (42.7%)
Synonym: Stibium

Occurrence and Uses

Antimony occurs in nature primarily in the mineral stibnite, and also in several other ores, such as valentinite, senarmontite, cervantite, kermasite, livingstonite, and jamisonite. It is also found in lead scraps from batteries.

Antimony alloys have many commercial applications. The metal makes its alloys hard and stiff and imparts resistance to corrosion. Such alloys are used in battery grids and parts, tank linings, pipes and pumps. The lead plates in the lead storage batteries constitute 94% lead and 6% antimony. Babbit metal, an alloy of antimony, tin, and copper is used to make antifriction machine bearings. Alloys made from very high purity grade antimony with indium, gallium and bismuth are used as infrared detectors, diodes, hall effect devices and thermoelectric coolers.

Physical Properties

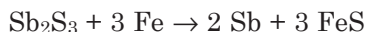
Silvery-white, brittle metallic element; crystal system-hexagonal, rhombohedral; also, exists in two unstable allotropic forms—a yellow modification and a dark-grey lustrous amorphous powder—both of which revert to crystalline form; hardness 3.0 to 3.5 Mohs; density 6.697g/cm³; melting point 630.5°C; boiling point 1635°C; electrical resistivity 39.1 microhm-cm at 0°C; magnetic susceptibility -0.87×10^{-6} emu/g.

Thermal Properties

Specific heat at 25°C	0.050 cal/g°C
Latent heat of fusion	38.5 cal/g
Latent heat of vaporization	161 cal/g
Coefficient of linear expansion at 25°C	$9 \times 10^{-6} / ^\circ\text{C}$
Thermal conductivity at 25°C	0.185 watts/cm°C

Production

Antimony is obtained from its ores, stibnite, Sb₂S₃ or tetrahedrite, 3Cu₂S · Sb₂S₃. The metal is recovered from high-grade stibnite by reduction with iron:



Alternatively, low-grade stibnite ore is converted to its oxide which is then reduced with carbon. Tetrahedrite may be treated with sodium sulfide solution. The solution containing thioantimonate formed is then electrolyzed in a diaphragm cell using a steel cathode and lead anode. The metal is further refined by oxidation or electrorefining process.

Sb may be made in the laboratory by reduction of antimony pentoxide with potassium cyanide.

Reactions

Antimony is stable in dry air and not readily attacked by moisture; slowly oxidized by moist air. Under controlled conditions oxidation may result forming tri-, tetra-, and pentaoxides; Sb₂O₃, Sb₂O₄ and Sb₂O₅, respectively.

Sb reacts with sulfur, combining in all proportions, forming tri-, and pen-

tasulfides, Sb_2S_3 and Sb_2S_5 , respectively.

Sb is oxidized by nitric acid, forming a gelatinous precipitate of hydrated antimony pentoxide. It does not react with cold dilute sulfuric acid. However, reaction occurs in hot concentrated acid: an oxysulfate of indefinite composition and low acid-solubility is formed. It reacts with hydrofluoric acid to form soluble antimony trifluoride and pentafluoride. Hydrochloric acid in the absence of air does not readily attack the metal; however, finely divided antimony reacts with hot concentrated acid forming chloride salt.

Sb reacts with chlorine or bromine forming antimony chloride or bromide; with iodine, the reaction occurs in boiling benzene or halogenated organic solvent to form antimony triiodide, SbI_3 .

Analysis

The metal may most conveniently be analyzed in the aqueous phase by atomic absorption spectrophotometry using flame or a graphite furnace or by ICP emission spectrophotometry at wavelength 206.83 or 217.58 nm. Such measurements are accurate at trace concentration levels. The metal or its ore is digested with hot nitric acid and the acid extract is appropriately diluted and measured.

ANTIMONY PENTACHLORIDE

[7647-18-9]

Formula SbCl_5 ; MW 299.02; the solid is a dimer of two SbCl_4 units attached by two bridging Cl atoms.

Synonym: antimony perchloride

Uses

Antimony pentachloride is used as a catalyst in organic synthesis.

Physical Properties

Colorless or yellow oily liquid; fumes in air; freezes at 2.8°C ; boils at 140°C with some decomposition; bp 85°C at 55 torr; density 2.336g/mL at 20°C ; refractive index 1.601; decomposes in water; soluble in hydrochloric acid, chloroform and carbon tetrachloride.

Thermochemical Properties

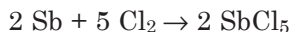
ΔH°_f	-105.2 kcal/mol
ΔG°_f	-83.7 kcal/mol
S°	72 cal/deg mol

Preparation

Antimony pentachloride is prepared by passing chlorine gas into molten antimony trichloride:

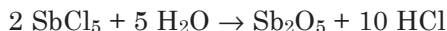


or by the reaction of the element with excess chlorine:



Reactions

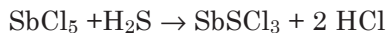
Antimony pentachloride hydrolyzes to antimony pentaoxide in excess water, forming HCl:



However, with calculated quantities of cold water or with moisture, monohydrate, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ and tetrahydrate, $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$ are formed. It reacts violently with many organics producing their chloro derivatives.

When added to a dilute solution of caustic soda or caustic potash, it forms $[\text{Sb}(\text{OH})_6]^-$ ion in the solution, from which the sodium or potassium salt, $\text{NaSb}(\text{OH})_6$ or $\text{KSb}(\text{OH})_6$ crystallizes out. It forms two adducts with ammonia, a red triammine, $\text{SbCl}_5 \cdot 3\text{NH}_3$, and a colorless tetraammine, $\text{SbCl}_5 \cdot 4\text{NH}_3$. SbCl_5 dissociates on heating to trichloride and chlorine; dissociation commencing around 120°C and completing at 300°C.

SbCl_5 reacts with H_2S forming antimony (V) thiochloride:



SbCl_5 undergoes vigorous reaction with carbon disulfide, producing carbon tetrachloride, antimony trichloride and sulfur:



Reaction with iodine forms iodine monochloride, ICl which combines with excess SbCl_5 to form adducts, $\text{SbCl}_5 \cdot 2\text{ICl}$ and $\text{SbCl}_5 \cdot 3\text{ICl}$; similarly reaction with chlorine trifluoride, ClF_3 gives antimony dichlorotrifluoride, SbCl_2F_3 .

Analysis

Elemental composition: Sb 40.72%, Cl 59.28%.

The compound is digested with nitric acid and the solution is analyzed for antimony by AA or ICP spectrophotometry (see Antimony). To determine the chlorine content a measured amount of substance is heated at 300°C and the liberated Cl_2 is passed into an acidic solution of KI and analyzed by iodometric titration using a standard solution of sodium thiosulfate or phenyl arsine oxide and starch indicator.

Hazard

Antimony pentachloride reacts explosively with phosphonium iodide, PH_4I (Mellor, J. W. 1947. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Oxford, UK: Longmans and Green) and explodes mildly when treated with oxygen difluoride at 150°C (Bretherick, L. 1995. *Handbook of Reactive Chemical Hazards*, 5th edition, ed. P.G.Urben, p. 1420. Oxford, UK:

Butterworth-Heinemann). The liquid is corrosive to skin. Exposure to its dust can cause irritation of upper respiratory tract and slightly delayed abdominal pain; the effect attributed to HCl produced upon contact with moist tissues (Cordasco, E.M. 1974. *Angiology*, 25, p. 590).

ANTIMONY PENTAFLUORIDE

[7783-70-2]

Formula SbF_5 ; MW 216.74; linear polymeric chains in liquid state and cyclic tetramer structures in solid phase associated with F bridging atoms. Such F bridges exist even in the gas phase (Passmore, J. 1985. *J Chem. Soc. Dalton Trans.*, p. 9)

Uses

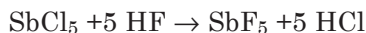
Antimony pentafluoride is used as a fluorinating agent for fluorination of organic compounds.

Physical Properties

Colorless oily liquid; highly viscous; hygroscopic; freezes at 8.3°C ; boils at 149.5°C ; density 2.99 g/cm^3 at 23°C ; soluble in excess water (with violent reaction) and glacial acetic acid; also soluble in potassium fluoride.

Preparation

Antimony pentafluoride is prepared by the reaction of antimony pentachloride with anhydrous hydrogen fluoride:



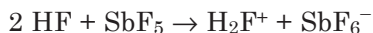
It may also be prepared from antimony trifluoride and fluorine, or by treating antimony pentaoxide with aqueous hydrofluoric acid and evaporating water.

Reactions

Antimony pentafluoride reacts with calculated amount of water forming a solid dihydrate, $\text{SbF}_5 \cdot 2\text{H}_2\text{O}$. The reaction is violent in excess water when the dihydrate dissolves forming a clear solution. It hydrolyzes slowly in caustic alkalies forming a hexacoordinated complex anion, $\text{Sb}(\text{OH})_6^-$. It reacts with organics forming their fluoro derivatives. It combines with iodine forming two dark-colored adducts, SbF_5I (m.p. 80°C) and $\text{Sb}_2\text{F}_{10}\text{I}$ (m.p. between 110°C to 115°C), both of which readily decompose in water. Similarly reaction with nitrosyl fluoride, NOF forms a stable adduct, NOSbF_6 . It forms mixed pentahalides, such as SbCl_4F , SbCl_3F_2 and SbCl_2F_3 . Sulfur dissolves in antimony pentafluoride forming a dark blue solution from which antimony thiopentafluoride, SbSF_5 crystallizes out.

Being a fluoride ion acceptor, SbCl_5 enhances the acidities of HF and HSO_3F solutions, forming SbF_6^- ion or more complex species. Thus, SbF_5 in

liquid HF gives a conducting solution as per the following equation:



(Cotton, A. F. and G. Wilkinson, 1988. *Advanced Inorganic Chemistry*, 5th Ed., p. 394, New York: John Wiley)

Analysis

Elemental composition: Sb 56.17%, F 43.38%

The compound is cautiously dissolved in nitric acid and the solution is appropriately diluted for the analysis of antimony by AA spectrophotometry or ICP emission spectrophotometry; and fluoride ion is determined by ion-selective electrode or ion chromatography.

Hazard

The liquid is corrosive to skin; vapors can cause respiratory tract irritation.

ANTIMONY PENTASULFIDE

[1315-04-4]

Formula Sb_2S_5 ; MW 403.82 indefinite composition; antimony occurs in the trivalent state containing a variable amount of sulfur.

Synonyms: golden antimony sulfide; golden sulfide of antimony; antimonie sulfide

Uses

Antimony pentasulfide is used in vulcanization of rubber to produce red rubber; in fireworks; and as a pigment.

Physical Properties

Orange-yellow or reddish amorphous powder; density 4.12 g/cm³; decomposes at 75°C; insoluble in water and alcohol; soluble in hydrochloric acid, caustic alkalies and ammonium hydrosulfide.

Preparation

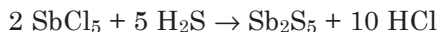
The compound is made commercially by converting antimony trisulfide to tetrathioantimonate by boiling with sulfur in caustic soda solution:



The sparingly soluble sodium antimonate is filtered out of the solution. The yellow-orange antimony pentasulfide precipitates out on treatment with hydrochloric acid.



It may also be prepared by the reaction of antimony pentachloride in HCl with hydrogen sulfide and removing any free sulfur by extraction with carbon disulfide:



Reactions

Antimony pentasulfide reacts with caustic soda forming soluble sodium thioantimonate, Na_3SbS_4 . It is sparingly soluble in sodium antimonate, NaSbO_3 . It forms a yellow solution with ammonia, and leaves a residue of antimony trisulfide, Sb_2S_3 and sulfur.

Analysis

Elemental composition: Sb 60.30%, S 39.70%

Antimony is analysed using AA or ICP spectrophotometry.

ANTIMONY PENTOXIDE

[1314–60–9]

Formula Sb_2O_5 ; MW 323.50; always occurs in hydrated form, $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$; commercial product is either hydrated Sb_2O_5 or $-\text{Sb}_2\text{O}_4$

Synonyms: antimony(V) oxide; antimonic acid (hydrated oxide)

Uses

Antimony pentoxide is used as an ion-exchange resin for a number of cations in acidic solution including Na^+ (especially for their selective retentions); and as a polymerization and oxidation catalyst.

Physical Properties

Yellow powdery solid; density 3.80 g/cm³; very slightly soluble in water; hydrated pentoxide is insoluble in nitric acid; dissolves in an aqueous solution of caustic potash.

Thermochemical Properties

ΔH°_f	–232.30 kcal/mol
ΔG°_f	–198.20 kcal/mol
S°	29.9 cal/deg mol

Preparation

The hydrated oxide is prepared by hydrolysis of antimony pentachloride; or by acidification of potassium hexahydroxoantimonate(V), KSb(OH)_6 [12208–13–8]. The product, filtered and air dried at ambient temperature has approximate composition $\text{Sb}_2\text{O}_5 \cdot 3.5\text{H}_2\text{O}$. It may be also prepared by oxidation of antimony trioxide with nitric acid.

Reactions

When heated at 700°C the yellow hydrated pentoxide converts to an anhydrous white solid with a formula Sb_2O_{13} containing both Sb(III) and Sb(V). Heating at 900°C produces a white insoluble powder of SbO_2 of both α and β forms. The β form consists of Sb(V) in octahedral interstices and pyramidal Sb(III) O_4 units.

Hydrated pentoxide reacts with metal hydroxides to form hydrated antimonate(V) salts, with the general formula $\text{M}(\text{SbO}_3)_2 \cdot 12\text{H}_2\text{O}$. In these compounds Sb(V) atom is octahedrally coordinated to six $-\text{OH}$ groups.

Treatment with NaOH solution produces sodium pyroantimonate, $\text{Na}(\text{H}_2\text{O})_6 [\text{Sb}(\text{OH})_6]_2$ [10049–22–6] and sodium hexahydroxo antimonate(V), $\text{Na}[\text{Sb}(\text{OH})_6]$ [12339–41–2]. Heating with metal oxides and carbonates produces various polyantimonate(V) derivatives.

ANTIMONY TRICHLORIDE

[10025–91–9]

Formula SbCl_3 ; MW 228.13; pyramidal molecular structure in the upper phase; Sb–Cl bond distance 2.38Å

Uses

Antimony trichloride is used as a catalyst for polymerization, hydrocracking and chlorination reactions; as a mordant; and in the production of other antimony salts. Its solution is used as an analytical reagent for chloral, aromatics and vitamin A.

Physical Properties

Colorless crystalline solid; orthorhombic crystal; hygroscopic; density 3.14 g/cm³; melts at 73.4°C; boils at 220.3°C; readily dissolves in water undergoing hydrolysis; soluble in dilute hydrochloric acid, ethanol, acetone, benzene, dioxane and CS_2 .

Thermochemical Properties

ΔH°_f	–91.4 kcal/mol
ΔG°_f	–77.4 kcal/mol
S°	44.0 cal/mol deg
C_p	25.8 cal/mol deg

Preparation

SbCl_3 is prepared by reaction of chlorine with antimony, antimony trioxide or antimony trisulfide. It also may be made by treating antimony trioxide with concentrated hydrochloric acid.

Reactions

Antimony trichloride hydrolyzes readily with water. With limited quantities of water and under carefully controlled conditions it becomes antimony chlo-

ride oxide, SbOCl , a butter-like mass, which is also formed when the trichloride picks up moisture from the air. A common hydrolysis product from partial hydrolysis is tetraantimony dichloride pentoxide, $\text{Sb}_4\text{O}_5\text{Cl}_2$, initially a thick white solid which changes to colorless crystal. Other partially hydrolyzed products include Sb_2OCl_4 , $\text{Sb}_4\text{O}_3(\text{OH})_3\text{Cl}_2$, $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ and $\text{Sb}_8\text{OCl}_{22}$. With excess water hydrous antimony oxide, $\text{Sb}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ is formed.

Heating with chlorine, or passing the gas into the molten trichloride yields antimony pentachloride, SbCl_5 . Reaction with HF produces trifluoride, SbF_3 .

SbCl_3 forms complexes with neutral donors. It also behaves as a Lewis acid forming chloroantimonate (III) ions, such as SbCl_4^- , SbCl_5^{2-} , SbCl_6^{3-} , $\text{Sb}_2\text{Cl}_7^{2-}$ etc., which are likely to form in the presence of metal ions and excess Cl^- ion. It forms a number of adducts with organic bases, such as, aniline and trimethylamine. Example of such adducts include $\text{SbCl}_3 \cdot \text{H}_2\text{NC}_6\text{H}_5$, $\text{SbCl}_3 \cdot (\text{CH}_3)_3\text{N}$, $2\text{SbCl}_3 \cdot (\text{CH}_3)_3\text{N}$, $\text{SbCl}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ and $\text{SbCl}_3 \cdot 2\text{CH}_3\text{COCH}_3$. It also forms 2:1 and 1:1 complexes with benzene, p-xylene, naphthalene and other aromatics, i.e., $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_6$ and $\text{SbCl}_3 \cdot \text{C}_6\text{H}_6$.

Antimony trichloride also behaves as a Lewis base. However, such reactions are very limited. They include the formation of carbonyl complexes $\text{Fe}(\text{CO})_3(\text{SbCl}_3)_2$ and $\text{Ni}(\text{CO})_3\text{SbCl}_3$.

Analysis

Elemental composition: Sb 53.37%, Cl 46.63%. The compound may be identified from its melting and boiling points. Antimony may be analyzed by AA or ICP spectroscopy. The trichloride may be hydrolyzed with limited quantities of water, the thick white precipitate turns to colorless crystals of $\text{Sb}_4\text{O}_5\text{Cl}_2$ which is separated and analyzed for elemental composition.

Health Hazard

The compound is corrosive to skin. Inhalation of its vapors can produce upper respiratory tract irritation, slightly delayed abdominal pain, and loss of appetite (Taylor, P. J. 1966. *Brit. J. Ind. Med.*, 23, p. 318).

ANTIMONY TRIOXIDE

[1309–64–4]

Formula Sb_2O_3 ; MW 291.50

Synonyms: antimony(III) oxide; antimony sesquioxide

Occurrence and Uses

Antimony trioxide occurs in nature as minerals, valentinite [1317–98–2] and senarmontinite [12412–52–1]. It is used as a flame retardant in fabrics; as an opacifier in ceramics, glass and vitreous enamels; as a catalyst; as a white pigment in paints; as a mortar in the manufacture of tartar emetic; and in the production of metallic antimony.

Physical Properties

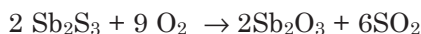
Occurs as colorless orthorhombic modifications, valentinite, or colorless cubic form, senarmontite; density 5.67 g/cm³ (valentinite), 5.20g/cm³ (senarmontite); cubic modification is dimeric consisting of Sb₂O₆ discrete molecules; refractive index 2.087; melts in the absence of oxygen at 656°C; boils at 1,550°C (sublimes); sublimes in vacuum at 400°C; very slightly soluble in water, insoluble in organic solvents; soluble in HCl, caustic alkalies and tartaric acid.

Thermochemical Properties

$\Delta H^{\circ}f$	-164.90 kcal/mol
H_{fus}	46.3 cal/g

Preparation

Antimony trioxide is obtained by roasting stibnite:

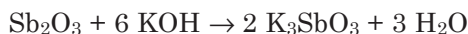


Temperature and air feed is carefully controlled in the process to suppress any formation of antimony tetroxide (Sb₂O₄). Antimony trioxide is separated from any arsenic trioxide (As₂O₃) that may be present as an impurity by volatilization, as the latter is much more volatile than the former. It may be also prepared by alkaline hydrolysis of antimony trichloride and subsequent dehydration of hydrous oxide under controlled heating (rapid or vigorous heating may partially oxidize Sb(III) to Sb(V)).

Antimony trioxide also may be made by heating the metallic element with oxygen or air. The volatilizing trioxide is condensed and collected.

Reactions

Antimony trioxide is an amphoteric oxide, exhibiting both acidic and basic behavior. It dissolves in strong acids forming antimony salts; e.g., reacts with aqueous hydrofluoric acid to form antimony trifluoride, SbF₃. It reacts with strong alkalies to form antimonites, such as sodium or potassium antimonites, Na₃SbO₃ or K₃SbO₃:



It is oxidized to antimony pentoxide, Sb₂O₅ on treatment with nitric acid; and forms potassium antimony tartrate (tartar emetic, K₂Sb(OH)₆ · C₄H₂O₆) when heated with acid potassium tartrate.

ANTIMONY TRISULFIDE

[1345-04-6]

Formula: Sb₂S₃; MW 339.72

Synonym: antimony sesquisulfide; antimony sulfide

Occurrence and Uses

Antimony trisulfide occurs in nature primarily as the mineral, stibnite, which consists of two parallel Sb_4S_6 chains linked together. It is used in fireworks; in certain types of safety matches; as a pigment in paints; and in the manufacture of ruby glass.

Physical Properties

Natural stibnite is black orthorhombic crystal; or grayish-black powder; the compound also exists as an amorphous substance in yellow-red modification; distorted octahedral arrangement; density 4.64 g/cm^3 for the natural stibnite and 4.12 g/cm^3 for the red modification; melts at 550°C ; vaporizes around 1150°C ; insoluble in water (1.75mg/L at 18°C) and acetic acid; soluble in hydrochloric acid and caustic soda solution; also, soluble in alcohol, ammonium hydrosulfide and potassium sulfide.

Thermochemical Properties

Black stibnite crystal

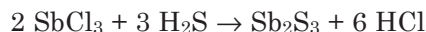
ΔH°_f	-41.8 kcal/mol
ΔG°_f	-41.5 kcal/mol
S°	43.5 cal/deg mol
C_p	$28.65 \text{ cal/deg mol}$

Red amorphous modification

ΔH°_f	-35.2 kcal/mol
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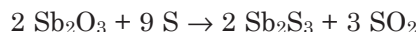
Preparation

The pure sulphide is obtained from its ore. Stibnite is separated from other ores by grinding and flotation. The ore is then heated to $550\text{--}600^\circ\text{C}$ in a perforated vessel. The pure molten material is collected and cooled. It is also prepared by passing hydrogen sulfide into a solution of antimony trichloride:



or treating antimony trichloride solution with sodium thiosulfate.

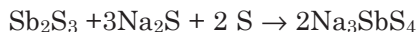
Alternatively, heating antimony metal or antimony trioxide with sulfur forms antimony trisulfide:



All these above preparative methods yield amorphous antimony trisulfide.

Reactions

Heating with sodium sulfide and sulfur or with sodium polysulfide produces sodium thioantimonate, Na_3SbS_4 (also, known as Schlippe's salt),



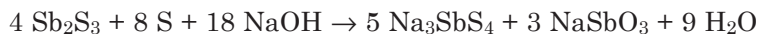
which on treatment with hydrochloric acid decomposes to antimony pentasulfide:



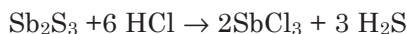
Heating with sodium sulfide alone forms sodium thioantimonite:



Sodium antimonate and thioantimonate are formed when a mixture of antimony trisulfide and sulfur are added to an excess boiling aqueous caustic soda solution:



It dissolves in and reacts with concentrated hydrochloric acid, liberating H_2S :



Analysis

Elemental composition: Sb 71.68%, S 28.32%

The compound is treated with concentrated HCl; H_2S is liberated and is identified from its odor; which also turns lead acetate paper black. The liberated H_2S is transported onto a GC port by helium carrier gas and determined by an FID, TCD or FPD. Antimony in the solution may be analyzed by flame or furnace AA or by ICP spectrophotometry. The solid powder may be characterized by X-ray diffraction technique.

ARGON

[7440-37-1]

Symbol Ar; atomic number 18; atomic weight 39.948; an inert gas element; electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$; 1st ionization potential 15.76eV; stable isotopes and natural abundance: Ar-40 99.6%, Ar-36 0.337%, Ar-38 0.063%; unstable isotopes, half-life and disintegration mode:

Ar-35	1.83sec	α -decay
Ar-37	35 days	electron capture
Ar-39	265 yr	β -decay
Ar-41	9.17 yr	β -decay
Ar-42	~3.5 yr	β -decay

Occurrence

The element was discovered by Lord Raleigh and Sir William Ramsay in 1894. Argon is the third most abundant element in the atmosphere. Its concentration in air is 0.934% by volume. Also, it occurs in earth's crust at a concentration of 3.4 mg/kg, and in the sea water at 4.3 $\mu\text{g/L}$. It was most likely formed in earth crust by radioactive decay of K-40 and seeped out into the

atmosphere. Argon-40 has been detected in the atmosphere of Mars, estimated to be about 1.6% by volume.

Uses

Argon has numerous applications in metallurgy, cryogenic, electronic, laboratory and as light sources. It is used in low-pressure gas discharge tubes as a filler gas, emitting bluish light. It is also used mixed with other inert gases in mercury- and sodium-vapor lamps. In metallurgy it is used to shield and protect welding metal arcs; in surface cleaning of metals; as a working fluid in plasma arc devices; as an inert blanket in melting and casting of certain alloys; to atomize molten metals and produce their powder; and in high-temperature soldering and refining operations; and powder metal sintering. In the laboratory, argon is used as a carrier gas for gas chromatography; or for metal analysis by furnace atomic absorption or inductively coupled plasma emission spectrophotometry; and as a filler gas (often mixed with other gas) in Geiger-Muller, proportional cosmic ray and scintillation counters. It is also used as inert atmosphere in glove boxes to carry out reactions and handling of air-sensitive substances.

Argon is used as a low-temperature cryogenic fluid for isothermal baths. It is also used in air sampling by condensing the air in a trap and subsequently analyzing organic pollutants. In electronic industry argon and helium are used as protective atmosphere and heat-transfer medium to grow single crystals of ultrapure semiconductors; and as diluents and carriers of dopant gases such as phosphine or arsine.

Physical Properties

Colorless and odorless gas; heavier than air, density of the gas 1.7838 g/L at 0°C and 1.394 g/L for the liquid at the normal boiling point; liquefies at -185.9°C; solidifies at -189°C; critical temperature -122.3°C; critical pressure 48.34 atm; density at critical point 0.536 g/ml; viscosity of the gas 226.4 micropoise at 25°C and 1 atm and that for the liquid 2.75 millipoise at the boiling point; sonic velocity 307.8 m/sec at 25°C and 1 atm; practically insoluble in water (5.6 cc/100 cc at 0°C or 100 mg/L at 0°C).

Thermochemical Properties

Heat of vaporization (At the normal boiling point)	1550 cal/mol
Heat of fusion (At the triple point)	283 cal/mol
Heat capacity, Cp	4.99 cal/deg mol

Manufacture

Air is the primary source of argon. Argon is obtained by liquefaction of air followed by separation from liquid oxygen and nitrogen by distillation. High purity-grade gas is made from the crude gas by passage over heated copper or by selective adsorption. An alternative purification process involves addition of hydrogen followed by catalytic combustion of trace oxygen in argon and

then reliquefaction of argon to remove excess hydrogen.

Chemical Properties

No true chemical compound of argon is known. Its hydrate has been characterized; so have the ion molecules, such as $(\text{ArH})^+$, $(\text{ArXe})^+$ or $(\text{ArKr})^+$ formed in electric discharge tubes. Unstable AgF [56617–31–3] is produced in excited state by electron-beam pumping or discharge pumping of argon and fluorine gas mixture. Also, it forms a clathrate with α -hydroquinone (see under Argon Hydroquinone Clathrate). None of these above products shows atoms chemically bonded to argon.

Analysis

Argon is analyzed by mass spectrometry (characteristic ion m/z 40) or by gas-solid chromatography. Its concentration can be increased by several times by selective adsorption over a suitable adsorbent followed by thermal desorption of the gas onto the GC injection port.

ARGON HYDROQUINONE CLATHRATE

[14343–01–2]

Argon forms a cage-type clathrate with α -hydroquinone where it fits into the small cage opening space or cavity of the hydroquinone structural unit. The diameter of the cage system is 0.42 nm. The molecular ratios of argon to hydroquinone in such nonstoichiometric inclusion substances are in the range 0.3 to 0.85 molecule of Ar for three molecules of hydroquinone (in a three-dimensional network), which is equivalent to a mass of 3.6 to 10.3 g argon per 100 g hydroquinone. The heat of formation is in the range 5.86 kcal/mol. Argon is adsorbed to hydroquinone by weak Van der Waal force and there is no evidence of any type of chemical bonding. The clathrate is stable at room temperature and atmospheric pressure and can be stored for several weeks without much loss of argon. It may be noted that the presence of argon in the clathrate cages stabilizes modification of the hydroquinone molecule, which otherwise is unstable itself.

ARSENIC

[7440–38–2]

Symbol As; atomic number 33; atomic weight 74.922; covalent radius As^{3+} 1.21 Å; electron configuration $[\text{Ar}] 4s^2 3d^{10} 4p^3$; a Group VA (Group 15) metalloid element; electronegativity 2.20 (Allred-Rochow type); principal valence states, +5, +3, 0, and –3; stable isotope As–75.

Occurrence

Arsenic is widely dispersed in nature: found in the minerals arsenopyrite, FeAsS ; orpiment, As_2S_3 ; realgar, As_2S_2 ; lollengite, FeAs_2 ; enargite, $\text{CuS} \cdot$

As₂S₅. Terrestrial abundance of this element is estimated to be 5 g/ton (Carapella (Jr), S. C. 1968. In *The Encyclopedia of the Chemical Elements*, ed. Clifford A. Hampel, pp. 29–33, New York: Reinhold Book Corp.).

Uses

The major uses are in metallurgy, primarily as an additive to lead, copper, brass and many lead-base bearing alloys to improve their mechanical and thermal properties. Small amounts are added to lead in the manufacture of lead shot to improve its sphericity; also added to lead-base cable sheathing and battery grid metal to improve hardness. Addition of very small quantities to copper enhances the corrosion resistance. It prevents cracking in brass.

Physical Properties

Steel-gray crystalline brittle metal; hexagonal crystal system; atomic volume 13.09 cc/g atom; three allotropes are known: namely, the α -metallic form, a black amorphous vitreous solid known as β -arsenic, and also a yellow allotrope. A few other allotropes may also exist but are not confirmed. Sublimes at 613°C when heated at normal atmospheric pressure; melts at 817°C at 28 atm; density 5.72 g/cc (β -metallic form) and 4.70 g/cm (β -amorphous form); hardness 3.5 Mohs; electrical resistivity (ohm-cm at 20°C) 33.3×10^{-6} (β -metallic polycrystalline form) and 107 (β -amorphous form); insoluble in water.

Thermal Properties

C _p	0.082 cal/g/°C
ΔH_{fus}	88.5 cal/g
ΔH_{subli}	102 cal/g
Coeff. linear expansion, 20°C	$4.7 \times 10^{-6}/^\circ\text{C}$

Manufacture

The metallic arsenic is obtained primarily from its mineral, arsenopyrite. The mineral is smelted at 650 to 700°C in the absence of air. However, the most common method of production of the metal involves reduction of arsenic trioxide, AsO₃ with charcoal. Arsenic trioxide is produced by oxidation of arsenic present in the lead and copper concentrates during smelting of such concentrates. The trioxide so formed, readily volatilizes and is collected in a dust flue system where further treatment and roasting can upgrade the trioxide content. The trioxide vapors are then condensed and further purified by pressure leaching and recrystallization techniques. It is then reduced with charcoal to give metallic arsenic.

Chemical Properties

Elemental arsenic is stable in dry air but exposure to moist air tarnishes its surface to a golden bronze color which converts to a black oxide on further exposure. Arsenic vapors react with oxygen to form arsenic trioxide (sesquioxide):



Ordinarily arsenic does not react with water, hydrogen, caustic soda or hydrochloric acid. However, in presence of an oxidant it reacts with concentrated HCl. In concentrated HCl solution it reacts with hydrogen sulfide to form a precipitate of yellow arsenic sulfide, As_2S_3 . It forms orthoarsenic acid, H_3AsO_4 on reaction with concentrated nitric acid and chlorinated water.

When heated with chlorine, bromine or iodine vapors arsenic forms the corresponding trihalides; however, with fluorine, arsenic pentafluoride, AsF_5 is produced. With sulfur it forms mixtures of sulfides, As_2S_3 , As_2S_2 and As_2S_5 in vitreous forms and varying proportions depending on the conditions of reactions.

Arsenic combines with electropositive metals to form their arsenides, i.e., Mg_3As_2 or AlAs .

Analysis

Microgram amounts may be measured by atomic absorption spectrophotometry either in flame or furnace mode. The metal is digested with nitric acid and converted to hydride vapors prior to flame AA determination. It may be determined over a much wider concentration range using inductively coupled plasma emission spectrometry. Also, it can be determined by neutron activation analysis, titration, gravimetry or by colorimetric techniques. Arsenic sample is treated with a strong HCl solution, distilled as trichloride, AsCl_3 . The trichloride is precipitated as silver arsenate which is dissolved in HNO_3 and titrated by Volhard method. In trivalent state the metal may be titrated with iodine, KMnO_4 or KBrO_3 . Trace quantities may be determined colorimetrically. The metal forms colored complex on treatment with diethyldithiocarbamate or molybdenum blue. Gravimetric methods may be applied to estimate arsenic in amounts greater than 1 mg. It may be precipitated as trisulfide by H_2S or as pentasulfide by treatment with thioacetamide and determined gravimetrically.

Toxicity

Elemental arsenic is much less toxic than its soluble compounds. Only its uncommon yellow allotrope is highly toxic. Inhalation of metal dusts can cause ulceration of nasal septum. Ingestion may produce systemic skin and gastrointestinal effects in humans. Arsenic and its compounds are human carcinogens producing liver tumors.

ARSENIC ACID

[7778-39-4]

Formula $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$; MW 150.95;

Synonyms: orthoarsenic acid, arsenic acid hemihydrate

Commercial arsenic acid is usually the orthoarsenic acid [7774-41-6] corresponding to the above hemihydrate formula. The aqueous solution of this acid behaves as a triprotic acid: the dissociation constants, K_1 , K_2 and K_3 being 5.6×10^{-3} , 1.7×10^{-7} and 3.0×10^{-12} , respectively. The meta and pyro forms

of the acid are also known, namely metaarsenic acid, HAsO_3 or As(OH)O_2 [10102-53-1] and the pyroarsenic acid, $\text{H}_4\text{As}_2\text{O}_7$ [13453-15-1]. All these forms are interconvertible. For example, orthoarsenic acid or its orthoarsenate salt is produced when the meta- or the pyro form is treated with cold water. Similarly heating at 100°C converts orthoarsenic acid to pyroarsenic acid. Further heating produces metaarsenic acid.

Physical Properties

Hygroscopic translucent crystals; density between 2 to 2.5 g/cm^3 ; melts at 35.5°C ; loses water when heated to 160°C ; highly soluble in cold water; soluble in alcohol, glycerol and alkalies.

Thermochemical Properties

ΔH°_f (H_3AsO_4 , solid)	-216.6 kcal/mol
ΔH°_f (H_3AsO_4 , aq)	-216.2 kcal/mol

Preparation

Arsenic acid is prepared by treating arsenic trioxide with concentrated nitric acid; or by combination of arsenic pentoxide with water. The latter reaction is very slow. It is also formed when meta- or pyroarsenic acid is treated with cold water.

Reactions

Arsenic acid reacts with metal salts forming their orthoarsenates, e.g., calcium orthoarsenate. Reaction with silver nitrate in neutral solution produces a chocolate-brown precipitate of silver orthoarsenate. It forms pyroarsenic acid (or pyroarsenate) on heating over 100°C . It is reduced to arsenous acid (or arsenites) when treated with reducing agents.

Toxicity

The solid or aqueous solution is highly toxic. Toxic symptoms are similar to other soluble arsenic compounds. See Arsenic.

ARSENIC PENTASULFIDE

[1303-34-0]

Formula: As_2S_5 ; MW 310.14;

Synonyms: diarsenic pentasulfide; arsenic (V) sulfide

Uses

Arsenic pentasulfide is used as pigment; and as a light filter in thin sheets.

Physical Properties

Yellow-brown glassy amorphous solid; sublimes on heating; decomposes around 500°C ; insoluble in cold water ($\sim 1.4\text{ mg/L}$ at 0°C); dissolves in alkalies and solutions of alkali metal sulfides, and in nitric acid.

Preparation

Arsenic pentasulfide is prepared by precipitation from an acidic solution of orthoarsenic acid, H_3AsO_4 , or arsenic pentachloride, AsCl_5 or any other soluble As(V) salt by passing hydrogen sulfide. It may be also prepared by heating a mixture of arsenic and sulfur, extracting the fused mass with ammonia solution and reprecipitating arsenic pentasulfide at low temperature by addition of HCl.

Reactions

Arsenic pentasulfide hydrolyzes in boiling water, giving arsenous acid, H_3AsO_3 and sulfur:



It oxidizes in air at elevated temperatures producing arsenic oxides, the products and yields of which depend on the air supply. In alkali metal sulfide solutions arsenic pentasulfide forms thioarsenate anion, $[\text{AsS}_4]^{3-}$ and its alkali metal salts, e.g., Na_3AsS_4 .

ARSENIC PENTOXIDE

[1303–28–2]

Formula: As_2O_5 ; MW 229.84;

Synonyms: arsenic(V) oxide; arsenic acid anhydride

Uses and Occurrence

Arsenic pentoxide is used to make colored glass; in fungicide formulations; in adhesive for metals; in wood preservatives; in dyeing and printing; and to prepare arsenates.

Physical Properties

White amorphous solid; deliquescent; density 4.32 g/cm^3 ; melts at 315°C ; dissolves slowly in water but is very soluble (230 g/100g at 20°C); also soluble in alcohol.

Thermochemical Properties

ΔH°_f	-221.2 kcal/mol
ΔG°_f	-187.1 kcal/mol
S°	$25.20 \text{ cal/deg mol}$
C_p	$27.86 \text{ cal/deg mol}$

Preparation

Arsenic pentoxide is prepared by dehydration of crystalline arsenic acid at 200°C or above. The former is made by treating arsenic metal or arsenious oxide with nitric acid. Also, the pentoxide can be prepared by the reaction of arsenic trioxide with oxygen under pressure.

Reactions

The aqueous solution of arsenic pentoxide is arsenic acid which probably corresponds to the hemihydrate formula $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$. See Orthoarsenic acid. It behaves as a triprotic acid forming various arsenate derivatives of metals.

Arsenic pentoxide loses oxygen on heating at 300°C , near its melting point, producing arsenic trioxide, As_2O_3 . It is an oxidizing agent, liable to react vigorously with reducible substances, i.e., it liberates chlorine from HCl .

Toxicity

Highly toxic, LD_{50} oral (rat): 8 mg/kg; carcinogenic.

ARSENIC SESQUISULFIDE

[1303–33–9]

Formula As_2S_3 ; MW 246.04;

Synonyms: arsenic trisulfide; arsenic sulfide; arsenous sulfide; king's gold; king's yellow; orpiment; yellow arsenic sulfide

Occurrence and Uses

Arsenic sesquisulfide occurs in nature as the mineral orpiment. It is used as a pigment; in the manufacture of infrared-transmitting glass; in semiconductors and photoconductors; in pyrotechnics; in linoleum and oil cloth; for the removal of hairs from hides; and as a reducing agent.

Physical Properties

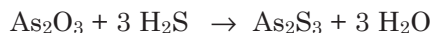
Yellow or orange monoclinic crystal or powder; a red allotrope modification also known; density 3.46 g/cm^3 ; melts at 310°C ; boils at 707°C ; insoluble in water; soluble in liquid ammonia and alkalis.

Thermochemical Properties

ΔH°_f	-40.41 kcal/mol
ΔG°_f	-40.32 kcal/mol
S°	$39.12 \text{ cal/deg mol}$
C_p	$27.81 \text{ cal/deg mol}$

Preparation

Arsenic sesquioxide may be prepared by heating arsenic trioxide with hydrogen sulfide:

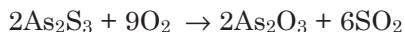


Alternatively, it may be precipitated out from a solution of arsenous acid or arsenic trioxide in dilute hydrochloric acid by passing hydrogen sulfide into the solution:

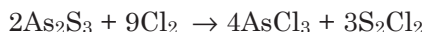


Reactions

Arsenic sesquisulfide burns in air giving arsenic trioxide and sulfur dioxide:



Reaction with chlorine produces arsenic trichloride and sulfur chloride:



When mixed with sodium sulfide solution it forms sodium dithioarsenite:



The reaction in polysulfide solution produces thioarsenate ion, AsS_4^{3-} . It is oxidized by common oxidants including nitric acid, hydrogen peroxide, ozone and permanganate undergoing vigorous to violent decomposition.

Analysis

Elemental composition: As 60.90%, S 39.10%. See Arsenic.

ARSENIC SULFIDE

[12279–90–2]

Formula As_4S_4 ; MW 427.95;

Synonyms: arsenic disulfide; arsenic monosulfide; red arsenic sulfide; ruby arsenic; realgar; red orpiment.

Occurrence and Uses

Arsenic sulfide occurs in nature as the mineral realgar. It is used as a pigment; in pyrotechnics to produce blue fire; in dyeing and calico printing; and as a depilatory for hides.

Physical Properties

Red monoclinic crystal; changes into a black allotropic modification at 267°C; density 3.50g/cm³; melts at 320°C; boils at 565°C; insoluble in water; soluble in alkalis.

Thermochemical Property

$$\Delta H^{\circ}f \quad -68.15 \text{ kcal/mol}$$

Preparation

Arsenic sulfide is prepared commercially by heating a mixture of iron pyrites and arsenopyrite; or by heating arsenic trioxide with sulfur. The com-

pound is then sublimed and collected. It may be also made from arsenic sesquisulfide – by either heating with sodium bicarbonate in a sealed tube or on prolong treatment with boiling solution of sodium carbonate.

Reactions

When heated in air at 800°C As_4S_4 vapors begin to dissociate to As_2S_2 which then ignites to form arsenic oxides. Ignition in chlorine produces arsenic chloride. Reaction with fluorine forms arsenic trifluoride. It is stable in water; and also in the air at ambient temperatures. It does not react with hot concentrated HCl but is decomposed by nitric acid. It forms thioarsenite ion, AsS_3^{3-} and elemental arsenic when warmed with caustic soda solution. Similar reaction occurs with sodium sulfide.

Analysis

Elemental composition: As 70.03%, S 29.97%. See Arsenic.

ARSENIC TRICHLORIDE

[7784–34–1]

Formula AsCl_3 ; MW 181.28; pyramidal structure; dipole moment in molecule in the gas phase 1.59 μD ; Synonym: arsenic (III) chloride; arsenic chloride

Uses

Arsenic trichloride is used in the preparation of many chloroderivatives of arsenic that have pharmaceutical and insecticide applications.

Physical Properties

Colorless oily liquid; fumes in air; density 2.163 g/ml at 20°C; refractive index 1.621 at 14°C; melts at 0.16°C; boils at 130.2°C; vapor pressure 9.75 torr at 25°C; decomposes in water; soluble in alcohol, ether, HCl and HBr.

Thermochemical Properties

ΔH°_f (liq)	–72.9 kcal/mol
ΔH°_f (gas)	–62.5 kcal/mol
ΔG°_f (liq)	–59.5 kcal/mol
S° (liq)	51.7 cal/deg mol
S° (gas)	78.17 cal/deg mol
C_p (liq)	18.10 cal/deg mol
ΔH_{vap}	8.9 kcal/mol

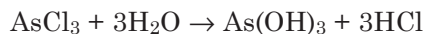
Preparation

The compound is generally made from arsenic trioxide by (i) passing chlorine over it or (ii) treating the trioxide with sulfur monochloride, S_2Cl_2 . Alternatively it is prepared from arsenic trioxide by distillation with either concentrated hydrochloric acid or a mixture of sulfuric acid and a metal chloride. Arsenic trichloride may also be prepared by combination of arsenic and

chlorine.

Reactions

Hydrolysis with water gives arsenous acid and HCl:



Reaction with potassium bromide or iodide forms arsenic tribromide or arsenic triiodide.

Analysis

Elemental composition: As 41.32%, Cl 58.68%. See Arsenic.

Toxicity

Highly toxic by all routes of exposure, LC₁₀ inhalation (cat): 100 mg/m³/1 hour; human carcinogen.

ARSENIC TRIFLUORIDE

[7784-35-2]

Formula AsF₃; MW 131.91

Physical Properties

Colorless oily liquid; fumes in air; etches glass; density 2.666 g/ml at 0°C; boils at 60.4°C; vapor pressure 100 torr at 13.2°C; solidifies at -8.5°C; decomposes in water; soluble in alcohol, ether, benzene and ammonia solution.

Thermochemical Properties

$\Delta H^\circ f(\text{liq})$	-196.3 kcal/mol
$\Delta H^\circ f(\text{gas})$	-187.8 kcal/mol
$\Delta G^\circ f(\text{liq})$	-184.0 kcal/mol
$S^\circ(\text{liq})$	43.31 cal/deg mol
$S^\circ(\text{gas})$	69.07 cal/deg mol
$C_p(\text{liq})$	30.25 cal/deg mol
$C_p(\text{gas})$	15.68 cal/deg mol

Preparation

The compound is prepared by reaction of arsenic trioxide with fluorosulfonic acid. Also it may be prepared by treating arsenic trioxide with a mixture of sulfuric acid and calcium fluoride.

Reactions

Arsenic trifluoride is hydrolyzed by water. It reacts with chlorine gas at ice-cold temperature to form arsenic dichloride trifluoride, AsCl₂F₃, a solid hygroscopic product that consists of the ions AsCl₄⁺ and AsF₆⁻.

It forms nitrosonium hexafluoroarsenate(V), [NO][AsF₆] with nitrosyl fluo-

ride; and a stable adduct with sulfur trioxide having the formula $2\text{AsF}_3 \cdot 3\text{SO}_3$.

Analysis

Elemental composition As 56.79%, F 43.21%. See Arsenic.

Toxicity

Highly toxic by all routes of exposure; LC₅₀ inhalation (mouse): 2000 mg/m³/10 min; a human carcinogen.

ARSENIC TRIIODIDE

[7784-45-4]

Formula AsI_3 ; MW 455.635; pyramidal molecule with covalent bonding; Synonym: arsenic (III) iodide; triiodoarsine; arsenous triiodide

Uses

Formerly the compound was used in dermatitides.

Physical Properties

Red solid; density 4.39 g/cm³ at 15°C; melts at 146°C; boils at 403°C; sparingly soluble in cold water (6 g/100 ml at 25°C), decomposes in hot water; readily dissolves in chloroform, benzene and toluene and moderately soluble in alcohol, ether and carbon disulfide (5.8%).

Thermochemical Properties

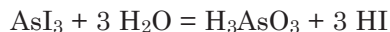
ΔH°_f	-13.9 kcal/mol
ΔG°_f	-14.2 kcal/mol
$S^\circ(\text{s})$	50.92 cal/deg mol
$S^\circ(\text{g})$	92.79 cal/deg mol
$C_p(\text{s})$	25.28 cal/deg mol
$C_p(\text{g})$	19.27 cal/deg mol

Preparation

Arsenic triiodide is prepared by treating elemental arsenic with a solution of iodine in carbon disulfide. Alternatively, it can be precipitated out from a hot solution of arsenic trioxide or arsenic trisulfide in hydrochloric acid on treatment with potassium or sodium iodide. Also, it is made by the reaction of arsenic trichloride with potassium iodide.

Reactions

Hydrolysis occurs slowly in water forming arsenic trioxide and hydriodic acid. The reaction proceeds via formation of arsenous acid which exists in equilibrium with HI:



The aqueous solution is highly acidic, pH of 0.1N solution is 1.1. It readily decomposes to arsenic trioxide, elemental arsenic and iodine when heated in air at 200°C. The decomposition, however, commences at 100°C:



Analysis

Elemental composition: As 16.44%, I 83.56%. See Arsenic.

Toxicity

Toxic and carcinogen.

ARSENIC TRIOXIDE

[1327–53–3]

Formula: As_2O_3 ; MW 197.82

Synonyms: arsenic oxide; arsenic sesquioxide; white arsenic; arsenic (III) oxide; arsenious acid anhydride

Uses

Arsenic trioxide is used as a starting material to prepare metallic arsenic and a number of arsenic compounds. It is also used as a decolorizer for bottle glass; in pigments and ceramic enamels; for preserving hides; as a wood preservative; as an analytical standard in oxidimetry titrations; and in many rodenticide and herbicide formulations.

Physical Properties

White crystalline solid; occurs in two modifications, namely, an octahedral or cubic form known as arsenolite and a monoclinic form, claudetite; arsenolite consist of dimeric, As_2O_6 arranged in a diamond-type lattice, subliming above 135°C and dissociating above 800°C to As_2O_3 ; density 3.86 and 3.74 mg/cm^3 for arsenolite and claudetite, respectively; melts at 274°C (arsenolite) and 313°C (claudetite); boils at 460°C; vapor pressure 5 torr at 234°C; sparingly soluble in cold water (1.7% at 25°C, dissolves very slowly), moderately soluble in boiling water (6.7%); soluble in dilute acids and alkalies; practically insoluble in organic solvents.

Thermochemical Properties

$\Delta H^\circ f$ (arsenolite)	–314 kcal/mol
$\Delta H^\circ f$ (claudetite)	–313 kcal/mol
S° (arsenolite)	51 cal/deg mol
S° (claudetite)	55 cal/deg mol

Preparation

Arsenic trioxide is obtained by roasting the mineral arsenopyrite, FeAsS , in air at 650 to 700°C. It is also obtained as a by-product during the smelting of

copper and lead concentrates during the extraction of these metals from their ores that contain arsenic. The latter readily oxidizes to arsenic trioxide which is volatilized. The vapors are then condensed and collected. High purity-grade oxide can be obtained by resublimation of the crude trioxide or by pressure leaching and recrystallization. Arsenic trioxide may also be prepared by hydrolysis of arsenic trichloride, -tribromide or -trifluoride.

Reactions

Arsenic trioxide dissolves in water to a slight extent, undergoing a slow hydrolysis reaction, forming weakly acidic orthoarsenous acid, $\text{As}(\text{OH})_3$.

Its solution exhibits amphoteric behavior. It dissolves in aqueous bases to give arsenite ions that have formulas, $[\text{AsO}(\text{OH})_2]^-$, $[\text{AsO}_2(\text{OH})]^{2-}$ and $[\text{AsO}_3]^{3-}$.

Arsenic trioxide reacts with oxygen under pressure to form arsenic pentoxide, As_2O_5 , a thermally unstable compound which dissociates around 300°C . It is oxidized by most common oxidizing agents including nitric acid, dichromate, permanganate, hypochlorite and iron(III) ion. Treatment with concentrated nitric acid produces arsenic acid, $\text{H}_3\text{AsO}_4 \cdot n\text{H}_2\text{O}$.

Arsenic trioxide is reduced by stannous chloride, SnCl_2 in HCl to arsenic monohydride, As_2H_2 , a brown amorphous powder.

Reactions with fluorine and chlorine give arsenic trifluoride AsF_3 and arsenic trichloride AsCl_3 , respectively.

Similarly, arsenic tribromide AsBr_3 forms when the trioxide reacts with bromine vapors. Reaction with concentrated HCl under heating produces arsenic trichloride.

Arsenic trioxide dissolves in concentrated H_2SO_4 forming arsenyl sulfate, $(\text{AsO}_2)_2\text{SO}_4$, a hygroscopic crystalline solid. Reaction with sulfur trioxide, SO_3 at 100°C produces arsenic trisulfate, $\text{As}_2(\text{SO}_4)_3$. It forms arsenic monosulfide, As_4S_4 when heated with sulfur.

Analysis

Elemental composition: As 75.74%, O 24.26%. See Arsenic.

Toxicity

Toxic by all routes of exposure and a carcinogen. Systemic effects from oral intake include muscle weakness, hypermotility, sleep change, diarrhea and cardiac arrhythmias. LD_{50} oral (rat): 14.6 mg/kg.

ARSENOUS ACID

[13464–58–9]

Formula H_3AsO_3 or $\text{As}(\text{OH})_3$; MW 125.94.

Arsenous acid is a weak acid, known to exist only in solution. Its molecule has three $-\text{OH}$ groups attached to the arsenic atom. The dissociation constant of this acid is 8.0×10^{-16} at 25°C . It is produced by hydrolysis of arsenic trioxide in water. The trioxide is sparingly soluble in water and the rate of

hydrolysis is generally slow, taking several hours before equilibrium is reached. It forms arsenite ions in aqueous bases, and all its reactions in the aqueous phases are those of arsenic trioxide (see Arsenic Trioxide).

ARSINE

[7784-42-1]

Formula AsH_3 ; MW 77.95;

Synonyms: arsenic trihydride; hydrogen arsenide

Uses and Occurrence

Arsine is used as a reducing agent; and to synthesize many organoarsine derivatives. It is also used as a doping agent for solid state electronic components. Earlier, it was used as a military poison gas. It does not occur freely in nature but is susceptible to form upon contact of arsenic compounds with acid in presence of a metal. Thus commercial acids stored in metal tanks and contaminated with arsenic impurities may produce arsine.

Physical Properties

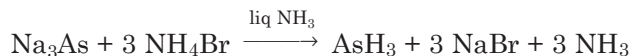
Colorless gas; garlic-like unpleasant odor; liquefies at -55°C ; solidifies at -116.3°C ; heavier than air; gas density 2.695 (air = 1); sparingly soluble in cold water (~ 20 mg/100 g water or about 640 mg/L at the NTP); soluble in chloroform and benzene.

Thermochemical Properties

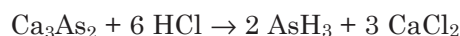
ΔH°_f	15.88 kcal/mol
ΔG°_f	16.47 kcal/mol
S°	53.22 cal/deg mol
C_p	9.10 cal/deg mol

Preparation

Arsine is produced by the reaction of arsenic trichloride, arsenic trioxide or any inorganic arsenic compound with zinc and sulfuric acid. It is also made by treating a solution of sodium arsenide or potassium arsenide in liquid ammonia with ammonium bromide:



It may be also prepared by decomposition of alkali metal arsenides by water; or arsenides of other metals with acids:

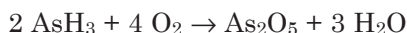
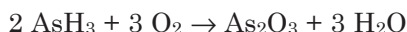
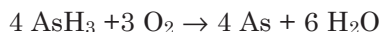


A poor yield may be obtained if water is substituted for acids. Thus calcium

arsenide reacts with water to produce about 15% arsine.

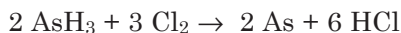
Reactions

Oxidation in air at elevated temperatures form arsenic along with arsenic trioxide or arsenic pentoxide, the nature of the product depending on the arsine to oxygen ratio:

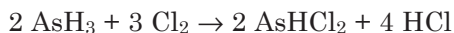
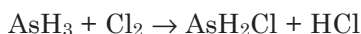


Such oxidation in air, however, does not occur at ordinary temperatures. Moist arsine decomposes readily in the presence of light forming deposits of shiny black arsenic. When heated in the absence of air it decomposes to its elements.

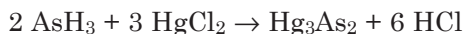
Arsine is a strong reducing agent, reducing many oxidizing agents, i.e., reduces chlorine to hydrogen chloride:



At low temperatures partial reduction of chlorine occurs, forming yellow unstable chloro derivatives, arsenic dihydrogen chloride and arsenic hydrogen dichloride:



Reaction with mercuric chloride gives mercuric arsenide, Hg_3As_2 :



Arsine reacts with cupric chloride solution to give cupric arsenide. Oxidation with stannic chloride, SnCl_4 , forms hydrogen diarsenide, As_4H_2 . It reacts with dilute silver nitrate solution forming metallic silver.

Arsine forms a hexahydrate, $\text{AsH}_3 \cdot 6\text{H}_2\text{O}$ at temperatures below -10°C or under pressure.

Analysis

Elemental composition: As 96.12%, H 3.88%. Arsine may be absorbed in potassium permanganate solution or in bromine water and the solution may be analyzed for arsenic by atomic absorption or emission spectrophotometry (see Arsenic). Alternatively arsine may be oxidized by moist air in presence of light to arsenic which may then be digested with nitric acid and determined as above.

Toxicity

Arsine is a dangerously acute toxicant and a carcinogen. Exposure to 250 ppm for 30 minutes can be fatal to human.

At lower concentrations toxic effects may manifest few hours after exposure. The symptoms include headache, weakness, dizziness, dyspnea, abdominal pain, nausea, vomiting and bronze skin. Chronic exposure can produce jaundice, hemolytic anemia and hemoglobinuria. PEL–TWA and TLV–TWA 0.05 ppm or 0.2 mg/m³ (OSHA and ACGIH).

ASTATINE

[7440–68–8]

Symbol At; atomic number 85; a radioactive halogen group element; electronic configuration [Xe]4f¹⁴5d¹⁰6s²6p⁵; most stable isotope At–210. The half-lives and decay modes of astatine isotopes are given below (Hyde, E. K., Perlman, I., and Seaborg, G. T. 1964. In *The Nuclear Properties of Heavy Elements*, Vol. II, pp. 1081–1082. Englewood Cliffs, NJ: Prentice-Hall);

At–200	0.8 min	α–decay
At–201	1.5 min	α–decay
At–202	3 min	electron capture (88%) α–decay (12%)
At–203	7.4 min	electron capture (86%) α–decay (14%)
At–204	9.3 min	electron capture (95.5%) α–decay (4.5%)
At–205	26 min	electron capture (82%) α–decay (18%)
At–206	29 min	electron capture (99.1%) α–decay (0.9%)
At–207	1.8 hr	electron capture (90%) α–decay (10%)
At–208	1.7 hr	electron capture (99.5%) α–decay (0.5%)
At–209	5.5 hr	electron capture (95%) α–decay (5%)
At–210	8.3 hr	electron capture (99.8%) α–decay (0.17%)
At–211	7.2 hr	electron capture (59%) α–decay (41%)
At–212	0.2 sec	α–decay
At–213	<1 sec	α–decay
At–214	0.002 sec	α–decay
At–215	10 ^{–4} sec	α–decay
At–216	3 x 10 ^{–4} sec	α–decay

At-217	0.018 sec	α -decay
At-218	2 sec	α -decay
At-219	0.9 min	α -decay (97%) β -decay (3%)

Occurrence

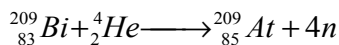
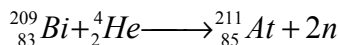
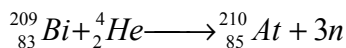
Astatine is one of the rarest elements in nature. Extremely small amounts of short-lived isotopes At-215, At-217, At-218 and At-219 are naturally found occurring in equilibrium with uranium, neptunium and thorium isotopes. The element was named by Corson, MacKenzie and Segre who produced the first of its isotope At-211 in 1940 by bombarding bismuth with alpha particles. Since then many isotopes in the mass range 200 to 219 have been synthesized. All isotopes, however, are unstable, their half-lives ranging between a few microseconds to less than ten hours. The most stable ones are At-210, At-211 and At-209. No use of this element is known so far.

Physical Properties

Physical properties of this element have not been well investigated due to short half-lives of isotopes. The element is volatile; may be distilled in vacuum at room temperature in a glass apparatus; and condensed in a dry ice trap. It is soluble in chloroform, ether, hexane and many other organic solvents. Solubility in water should be of low order.

Synthesis

The more stable astatine isotopes may be synthesized in a nuclear reactor by bombarding bismuth with energetic alpha particles:



The isotopes formed are distilled out from target by heating in air. Isotopes of low masses may be synthesized from other nuclei, i.e., fusion of gold and carbon atoms.

Reactions

Reactions of astatine should be similar to that of iodine. However, there is no evidence of existence of diatomic molecule, At₂. In aqueous solution it is known to exist in oxidation states -1, 0, +5 and +7 and several compounds or polyanions are known. Such species include HAt; interhalogen compounds AtCl, AtBr and AtI; polyhalide complex ions AtCl₂⁻, AtI₂⁻, AtIBr⁻, AtICl⁻ and AtBr²⁺; astatine anion AtO³⁻ and several organic compounds such as C₆H₅At, C₆H₅AtCl₂, At(C₃H₅N)₂ClO₄, *p*-AtC₆H₄COOH and HOC₆H₄At.

Analysis

The element may be determined from its radioactivity using tracer techniques. Isotopes of the element may be identified by mass spectrometry.

Health Hazard

Exposure to radiation may cause cancer. Studies on experimental animals show it induces tumors.

BARIUM

[7440-39-3]

Symbol Ba; atomic number 56; atomic weight 137.327; a Group IIA (Group 2) alkaline earth element; electronic configuration $[\text{Xe}]s^2$; valence state +2; ionic radius of Ba^{2+} in crystal (corresponding to coordination number 8) 1.42 Å; first ionization potential 10.00eV; stable isotopes and their percent abundances: Ba-138 (71.70), Ba-137 (11.23), Ba-136 (7.85), Ba-135 (6.59), Ba-134 (2.42); minor isotopes: Ba-130 (0.106) and Ba-132 (0.101); also twenty-two radioisotopes are known.

Occurrence

Barium was discovered in 1808 by Sir Humphrey Davy. Its abundance in the earth's crust is about 0.0425% (425 mg/kg). The element also is found in sea water at trace concentration, 13 µg/L. It occurs in the minerals barite or heavy spar (as sulfate) and witherite (as carbonate).

Uses

The most important use of barium is as a scavenger in electronic tubes. The metal, often in powder form or as an alloy with aluminum, is employed to remove the last traces of gases from vacuum and television picture tubes. Alloys of barium have numerous applications. It is incorporated to lead alloy grids of acid batteries for better performance; and added to molten steel and metals in deoxidizing alloys to lower the oxygen content. Thin films of barium are used as lubricant suitable at high temperatures on the rotors of anodes in vacuum X-ray tubes and on alloys used for spark plugs. A few radioactive isotopes of this element find applications in nuclear reactions and spectrometry.

Physical Properties

Silvery-white metal; soft and ductile; density 3.51 g/cm³; melts at 727° C; vaporizes at 1897°C; vapor pressure 0.1 torr at 730°C; electrical resistivity 34.0 microohm-cm at 25°C; reacts with water.

Thermochemical Properties

$\Delta H^{\circ}f$ (cry)	0.0	kcal/mol
$\Delta H^{\circ}f$ (gas)	43.04	kcal/mol
$G^{\circ}f$ (gas)	34.93	kcal/mol
S° (gas)	40.70	cal/degree mol
C_p (gas)	4.97	cal/degree mol

Manufacture

The metal is obtained by the reduction of barium oxide with finely divided

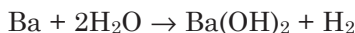
aluminum at temperatures between 1,100 to 1,200°C:



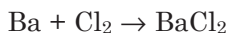
Barium vapor is cooled by means of a water jacket and condensed into the solid metal. The solid block may be cast into rods or extruded into wires. Being a flammable solid, it is packaged under argon in steel containers or plastic bags.

Reactions

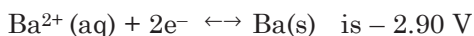
Barium metal reacts exothermically with oxygen at ambient temperatures forming barium oxide. The reaction is violent when the metal is present in powder form. It also reacts violently with water forming barium hydroxide and liberating hydrogen:



Barium reacts violently with dilute acids, evolving hydrogen. Reactions with halogens give barium halides:

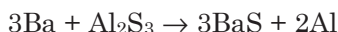
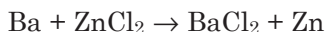
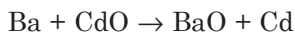


Barium is a strong reducing agent. The E° for the reaction:



It reduces oxidizing agents reacting violently. The metal combines with nitrogen and hydrogen at elevated temperatures producing barium nitride, Ba_3N_2 , and barium hydride, BaH_2 , respectively.

Barium reduces oxides, chlorides and sulfides of less reactive metals producing the corresponding metals; e.g.,



When heated with nitrogen in the presence of carbon, it forms barium cyanide:



Barium combines with several metals including aluminum, zinc, lead, and tin, forming a wide range of intermetallic compounds and alloys.

Hazard

The finely divided powder is pyrophoric. It can explode in contact with air

or oxidizing gases. It is likely to explode when mixed and stirred with halogenated hydrocarbon solvents. It reacts violently with water.

All barium salts, especially the water and acid-soluble compounds, are highly toxic. Barium ion can cause death through ventricular fibrillation of the heart. It is a stimulant to the heart muscle. Intake of a few grams of barium salt can be lethal to humans. The insoluble salts such as barium sulfate, however, have little toxic action.

Analysis

The metal may be analyzed in the solid matrices by x-ray fluorescence or x-ray diffraction, and neutron activation techniques. Trace quantities in solution may be measured by flame or furnace atomic absorption spectrophotometry or by ICP emission technique. Measurements at further lower concentrations may be made by an ICP, coupled with a mass spectrometer (ICP/MS). Also, barium ion in solution may be measured by various wet methods, including gravimetry and volumetric analysis. In gravimetry, the metal is precipitated in slightly acidic solution as insoluble sulfate or chromate. Complexometric titration using the complexing agent, diethylenetriamine-pentaacetic acid, and Eriochrome Black T as indicator, measures calcium and strontium along with barium and, therefore, is not suitable to analyze barium in a mixed solution.

BARIUM ACETATE

[543–80–6]

Formula: $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$; MW 255.42

Uses

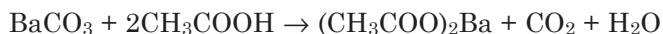
Barium acetate is used as a mordant for printing textile fabrics; for drying paints and varnishes; in lubricating oil; in the preparation of other acetates; and as a catalyst in organic synthesis.

Physical Properties

White powdery solid; density 2.47 g/cm³; decomposes on heating; highly soluble in water (55.8 g /100g at 0°C), sparingly soluble in methanol (~1.43 g per liter).

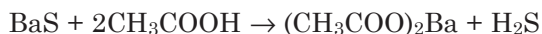
Preparation

Barium acetate is made by the reaction of barium carbonate with acetic acid:



The solution is concentrated and the anhydrous barium acetate crystallizes at a temperature above 41°C. At temperatures between 25 to 40°C, barium acetate monohydrate, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ [5908–64–5] (density 2.19 g/cm³) crystallizes out of solution.

Barium acetate also may be prepared by treating barium sulfide with acetic acid, followed by slow evaporation and subsequent crystallization of the salt from the solution:



Reactions

Barium acetate converts to barium carbonate when heated in air at elevated temperatures. Reaction with sulfuric acid gives barium sulfate; with hydrochloric acid and nitric acid, the chloride and nitrate salts are obtained after evaporation of the solutions. It undergoes double decomposition reactions with salts of several metals. For example, it forms ferrous acetate when treated with ferrous sulfate solution and mercurous acetate when mixed with mercurous nitrate solution acidified with nitric acid. It reacts with oxalic acid forming barium oxalate.

Analysis

Elemental composition: Ba 53.77%, C 18.81%, H 2.37%, O 25.05%. The salt may be digested with nitric acid, diluted appropriately, and analyzed for barium. (See Barium.)

Toxicity

The salt or its aqueous solution is highly toxic. LD₁₀ (oral) rabbit: 236 mg/kg; LD₁₀ (subcutaneous) rabbit: 96 mg/kg. See Barium.

BARIUM AZIDE

[18810-58-7]

Formula: Ba(N₃)₂; MW 221.37

Uses

Barium azide is used in explosives. A saturated solution is generally used.

Physical Properties

Colorless monoclinic crystal; density 2.936 g/cm³; decomposes at 120°C; soluble in water, slightly soluble in ethanol.

Preparation

Barium azide may be prepared by reacting sodium azide with a soluble barium salt. The solution is concentrated to allow crystals grow. Crystals will explode if fully dried, or subject to friction. Product should be stored damp with ethanol.

Hazard

The dry solid is sensitive to shock, impact and friction. It decomposes explosively when heated to 275°C. Contact with acid can produce the explo-

sive compound hydrazoic acid. Contact with lead, silver, and many other metals can form the explosive azides of those metals. Presence of sodium, potassium, barium and iron ions as impurities can enhance the shock sensitivity of barium azide. Barium azide also is a toxic compound. The toxic effects are similar to those of other soluble salts of barium.

BARIUM BROMIDE

[10553-31-8]

Formula: BaBr₂; MW 297.14

Uses

Barium bromide is used to make photographic compounds, phosphors, and other bromides.

Physical Properties

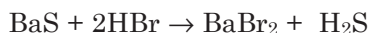
White orthorhombic crystal; density of anhydrous BaCl₂ 4.78 g/cm³, and dihydrate BaCl₂ · 2H₂O 3.58 g/cm³; melts at 857°C; vaporizes at 1,835°C; readily dissolves in water (92.2 g/100 g water at 0°C)

Thermochemical Properties

$\Delta H^{\circ}f$ (gas)	-181.1 kcal/mol
G° (gas)	-176.2 kcal/mol
S° (gas)	34.9 cal/degree mol
ΔH_{fus}	7.64 kcal/mol

Preparation

Barium bromide is prepared by the reaction of barium carbonate or barium sulfide with hydrobromic acid:



The white crystal of the dihydrate, BaBr₂ · 2H₂O is crystallized from aqueous solution. The anhydrous salt is obtained by heating the dihydrate at 120°C.

Reactions

Reactions in aqueous phase are similar to those of barium chloride. When treated with sulfuric acid, hydrofluoric acid, phosphoric acid or oxalic acid, the insoluble barium salts of these anions are formed. Similarly, many insoluble barium salts may form by double decomposition reactions when treated with soluble salts of other metals.

Analysis

Elemental composition: Ba 46.22%, Br 53.78%. Barium may be determined by various instrumental or wet methods (see Barium). Bromide may be analyzed by ion chromatography or titrimetry. Presence of other halide ions can interfere in titrimetry tests.

Toxicity

Ingestion of the salt or its aqueous solution can produce severe poisoning.

BARIUM CARBONATE

[513-77-9]

Formula: BaCO_3 ; MW 197.37

Occurrence and Uses

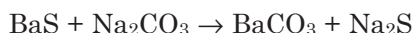
Barium carbonate is found in nature as mineral witherite. The compound has many major commercial applications in brick, glass, ceramics, oil-drilling, photographic and chemical industries. It is mixed with wet clay to immobilize many water-soluble salts in making uniform red bricks. In the glass industry, barium is added to glass as barium carbonate or barium oxide to improve the refractive index of optical glass; also to promote sintering and lower the viscosity of melted glass to make glass bead formation easy. It is used in the manufacture of television picture tubes and photographic paper. Another important application involves its use as a fluxing ingredient in ceramic industry for enamels, glazes and ceramic bodies. Barium carbonate is used in oil-well drilling to insolubilize gypsum and inhibit coagulation; in ferrous metallurgy for steel carburizing; in chlor-alkali cells for treating salt brines to remove sulfates; and to make ferrite, and barium titanate. Many barium salts are prepared from barium carbonate.

Physical Properties

White powder; orthorhombic crystal system; density 4.286 g/cm³; refractive index 1.60; hardness 3.50 Mohs; melts at 811°C; insoluble in water (c. 25 mg/L at 25°C); K_{sp} 2.0×10^{-9}

Manufacture

Barium carbonate is made commercially from barium sulfide either by treatment with sodium carbonate at 60 to 70°C (soda ash method) or by passing carbon dioxide at 40 to 90°C:



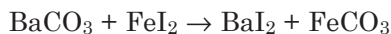
In the soda ash process, solid or dissolved sodium carbonate is added to bari-

um sulfide solution, and the barium carbonate precipitate is filtered, washed, and dried.

Reactions

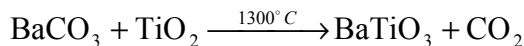
Barium carbonate decomposes to barium oxide and carbon dioxide when heated at 1,300°C. In the presence of carbon, decomposition occurs at lower temperatures. Barium carbonate dissolves in dilute HCl and HNO₃ liberating CO₂. Similar reaction occurs in acetic acid. The solid salts, chloride, nitrate and acetate that are water soluble may be obtained by evaporation of the solution. Dissolution in HF, followed by evaporation to dryness, and then heating to red heat, yields barium fluoride.

Barium carbonate forms barium iodide on treatment with ferrous iodide solution:



Barium carbonate produces barium potassium chromate, a pale yellow pigment, known as Pigment E, when heated with potassium dichromate.

Calcination at 1,300°C with titanium dioxide yields barium metatitanate, BaTiO₃:



Analysis

Elemental composition: Ba 69.58%, C 6.09%, O 24.32%. The compound is digested with nitric acid under heating and the solution is analyzed for barium by atomic absorption or emission spectrometry (see Barium). Carbon dioxide may be determined by treating a small amount of the solid with dilute HCl and analyzing the evolved gas by GC using a thermal conductivity detector or a mass spectrometer. The characteristic mass of CO₂ is 44.

BARIUM CHLORIDE

[10361–37–2]

Formula BaCl₂; MW 208.23; also forms a dihydrate, BaCl₂·2H₂O [10326–27–9]

Uses

Barium chloride is used to make red pigments and color lakes. Two such common pigments are Lithol Red [50867–36–2] and Red Lake C [5160–02–1]. It is used for weighting and dyeing textile fabrics and as a mordant for acid dyes. Other commercial uses of this compound include its application as an ingredient in eutectic mixtures for heat-treating baths; for tanning leather; as a flux in the production of magnesium metal; for softening of water in boilers; in additives for lubricating oils; and as a reagent for sulfate analysis by wet methods. It may be used to prepare other barium salts.

Physical Properties

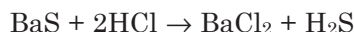
White crystal or powder; (crystal systems: anhydrous BaCl_2 is orthogonal, transition to cubic form occurs at 925°C , and the dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is monoclinic); hygroscopic; bitter, salty taste; density 3.856 g/cm^3 (dihydrate $3.0979/\text{cm}^3$); melts at 962°C ; vaporizes at $1,560^\circ\text{C}$; readily dissolves in water; also dissolves in methanol, but is insoluble in other polar organic solvents.

Thermochemical Properties

$\Delta H^\circ f$	-205.3 kcal/mol
$\Delta G^\circ f$	-193.8 kcal/mol
S°	$29.6 \text{ cal/degree mol}$
C_p	$17.9 \text{ cal/degree mol}$

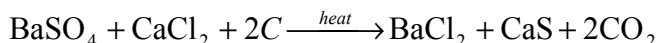
Manufacture

Barium chloride usually is prepared by treatment of barium sulfide with hydrochloric acid:



Impurities such as heavy metal sulfides are filtered out. Water-soluble sulfur compounds are oxidized to insoluble barium sulfate and removed. The solution is then evaporated to crystallize barium chloride.

Barium chloride may also be made by treating barium carbonate with HCl ; or by heating a mixture of barium sulfate, calcium chloride and carbon:

**Reactions**

Anhydrous barium chloride adsorbs moisture forming dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The latter forms a monohydrate, $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ when shaken with methanol. In an aqueous solution with sulfuric acid it forms a precipitate of barium sulfate. Similar precipitation reactions occur with hydrofluoric acid, arsenic acid, phosphoric acid and oxalic acid forming sparingly soluble barium fluoride, BaF_2 , and insoluble barium arsenate, $\text{Ba}_3(\text{AsO}_4)_2$, barium phosphate, $\text{Ba}_3(\text{PO}_4)_2$, and barium oxalate, BaC_2O_4 , respectively. Reactions with alkali metal carbonate, molybdate, niobate, selenate, ferrocyanide and hexafluoro-silicate produce insoluble barium salts of these anions. Anhydrous barium chloride forms lower melting eutectics with alkali metal chlorides.

Analysis

Elemental composition: Ba 65.95%, Cl 34.05%. The metal may be analyzed by various instrumental and wet methods (see Barium). Chloride ion may be determined in an aqueous solution of the salt by ion chromatography or by titrimetry using either silver nitrate titrant and an indicator such as potassi-

um chromate; or by mercuric nitrate titration using diphenyl carbazone indicator to detect the end point.

Toxicity

The acute toxicity is high by all routes of exposure. The effects are similar to other soluble compounds of barium (see Barium). The oral and subcutaneous lethal doses in dogs are as follows: (R. N. Lewis (Sr.). 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed., New York: Van Nostrand Reinhold.)

LD ₅₀ oral (dog):	90mg/kg
LD ₅₀ subcutaneous (dog):	10 mg/kg

BARIUM CHROMATE(VI)

[10294–40–3]

Formula: BaCrO₄; MW 253.32; Cr occurs in +6 oxidation state.

Synonyms: lemon yellow; permanent yellow; C.I. Pigment yellow 31; Baryta yellow; ultramarine yellow; C. I. 77103; Steinbuhl yellow.

Uses

Barium chromate is used as a pigment in paints, ceramics, coloring glasses, fuses, and porcelains; as a corrosion inhibitor to prevent electrochemical corrosion at the joints of dissimilar metals; in safety matches; in metal primers; in ignition control devices; in pyrotechnic compositions; and as an initiator for explosives.

Physical Properties

Yellow orthorhombic crystal; density 4.50 g/cm³; darkens on heating; insoluble in water and organic solvents; dissolves in mineral acid with decomposition.

Analysis

Elemental composition: Barium: 54.21%, chromium 20.53%, oxygen 25.26%. The compound is digested in nitric acid, diluted, and analyzed for barium and chromium by flame- or furnace-AA or ICP-AES (see Barium and Chromium). Also, it may be characterized by x-ray diffraction, and the metal content determined by other x-ray techniques.

Toxicity

Barium chromate is a toxic substance and an EPA-confirmed human carcinogen.

BARIUM CYANIDE

[542–62–1]

Formula: Ba(CN)₂; MW 189.36**Uses**

Barium cyanide is used in electroplating and other metallurgical processes.

Physical Properties

White crystalline powder; slowly decomposes in air; highly soluble in water, soluble in alcohol.

Preparation

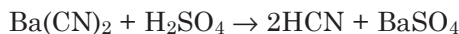
Barium cyanide is prepared by reacting barium hydroxide with hydrocyanic acid:



The product is crystallized from the solution.

Reactions

Barium cyanide reacts with acids producing hydrogen cyanide:



Ba(CN)₂ can form many insoluble cyanides from double decomposition reactions.

Analysis

Elemental composition: Ba 72.52%, C 12.68%, N 14.79%. Barium metal can be analyzed by various instrumental and wet methods (see Barium). Cyanide ion in the aqueous solution of the compound may be determined by using a cyanide ion-specific electrode or by colorimetry using pyridine-barbituric acid reagent (APHA, AWWA, and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed., Washington, DC: American Public Health Association).

Toxicity

Barium cyanide is a deadly poison. Ingestion of a small amount can cause death.

BARIUM HYDROXIDE

[17194–00–2]

Synonyms: caustic baryta; barium hydrate

Formula $\text{Ba}(\text{OH})_2$

Uses

Barium hydroxide is used to produce barium soaps which are additives for high temperature lubricants. Other chemical applications include refining of vegetable oils; vulcanization of synthetic rubber; in drilling fluids; in corrosion inhibitors; as an ingredient in sealing compositions; in plastics stabilizers; for softening water; and to prepare other alkalies.

Physical Properties

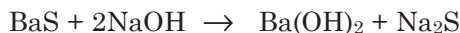
Monohydrate, $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is a white powder; density 3.743 g/cm^3 ; slightly soluble in water; soluble in dilute mineral acids. Octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is a colorless monoclinic crystal; density 2.18 g/cm^3 at 16°C ; refractive index 1.50; melts at 78°C ; vapor pressure 227 torr; loses seven molecules of water of crystallization when its solution is boiled in the absence of atmospheric CO_2 forming solid monohydrate; further heating produces anhydrous $\text{Ba}(\text{OH})_2$ melting at 407°C ; readily dissolves in water (3.76 g/100 g at 20°C and 11.7 g/100 g at 50°C); aqueous solution highly alkaline; also soluble in methanol; slightly soluble in ethanol; insoluble in acetone.

Thermochemical Properties

ΔH°_f	-225.9 kcal/mol
ΔH_{fus}	3.99 kcal/mol

Preparation

Barium hydroxide is made by dissolving barium oxide in hot water. The octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, crystallizes upon cooling. It also is prepared by precipitation with caustic soda from an aqueous solution of barium sulfide:



Reactions

Barium hydroxide decomposes to barium oxide when heated to 800°C . Reaction with carbon dioxide gives barium carbonate. Its aqueous solution, being highly alkaline, undergoes neutralization reactions with acids. Thus, it forms barium sulfate and barium phosphate with sulfuric and phosphoric acids, respectively. Reaction with hydrogen sulfide produces barium sulfide. Precipitation of many insoluble, or less soluble barium salts, may result from double decomposition reaction when $\text{Ba}(\text{OH})_2$ aqueous solution is mixed with many solutions of other metal salts.

Analysis

Elemental composition: Ba 80.15%, H 1.18%, O 18.67%. (See Barium.)

Toxicity

An acute poison; toxic symptoms are similar to other soluble salts of barium (see Barium).